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Energy Conservation— The First Law of Thermodynamics

What is thermodynamics? Very briefly, it is the study of energy and its transformations. We can also say immediately that all of thermodynamics is contained implicitly within two apparently simple statements called *the First and Second Laws of Thermodynamics.* If you know anything about these laws, you know that they have to do with energy—the first, explicitly, and the second, implicitly. The First Law says that energy is conserved. That's all; you don't get something for nothing. The Second Law says that even within the framework of conservation, you can't have it just *any* way you might like it. If you think things are going to be perfect, forget it. The Second Law invokes a quantity called *entropy*, something that is not part of our experience, so we'll let it go for a time and consider first the First Law. There is a certain logic in taking up the first things first, and furthermore it allows us to deal with something we all know about, namely, energy.

What is energy? One might expect at this point a nice clear, concise definition. Pick up a chemistry text, a physics text, or a thermodynamics text, and look in the index for "Energy, definition of," and you find no such entry. You think this may be an oversight; so you turn to the appropriate sections of these books, study them, and find them to be no help at all. Every time they have an opportunity to define energy, they fail to do so. Why the big secret? Or is it presumed you already know? Or is it just obvious?

For the moment, I'm going to be evasive too, but I'll return to the question. Whatever it *is*, one thing we know about energy is that it is conserved. That's just another way of saying that we believe in the First Law of Thermodynamics. Why do we believe in it? Certainly no one has proved it. On the other hand, no one has been able to find anything wrong with it. All we know is that it has always worked in every instance where it has been applied, and we are happy with it simply because it works. Why does it work? We haven't the faintest idea; it's just a miracle of nature. The conservation law is a *description* of how nature works, not an *explanation*. Fortunately that's all we need.

Although we do not know why it works, we do know how it works. Any conservation law says that something doesn't change, and any use of the law just involves accounting. We know there is a fixed amount of something, and we need merely find the various pieces that add up, or account for, the total. To give you an idea of how this is done, I am going to tell a ridiculous story. I've stolen the idea of this story from Richard Feynman, Nobel Prize-winning physicist and professor at the California Institute of Technology.

His "Lectures on Physics"[1] should be studied by every serious student of science and technology.

It is the story of 37 sugar cubes, a small boy, and his mother. To set the scene, I will ask you to imagine the boy's room at a corner of a house in rural surroundings. The room has two windows, one facing west and the other facing north. For identification, we will call them window W (for west) and window Q (sorry about that). It happens that window W overlooks a small pond. The boy (perhaps his name is Dennis) plays in this room, and his mother looks in from time to time. One day he asks his mother for some blocks to play with. She has no blocks, but she decides that sugar cubes will do. So she gives him 37 sugar cubes and tells him he is not to eat any or he'll be punished. Each time she returns to the room she counts the sugar cubes lying around, and they total 37; so all is well. But one day she counts and finds only 35. Now Dennis points to an old cigar box he plays with, and his mother starts to open it. But Dennis screams and says, "Don't open the box". The mother, of course, realizes she could open the box anyway, but she's an intelligent, modern mother, and she realizes that this would be a traumatic experience for the boy; so she takes another course.

Later in the day, when she again sees 37 sugar cubes lying about, she weighs the empty box, getting a value of 4.34 oz. She also weighs a sugar cube, getting a value of 0.12 oz. Now the clever lady sets up a formula by which she can check the number of sugar cubes:

$$\text{No. on floor} + \frac{\text{wt of box} - 4.34\text{ oz}}{0.12\text{ oz}} = 37$$

This formula works perfectly for quite a time. The left side always totals 37. But one day it does not. Two sugar cubes

[1] Addison-Wesley Publishing Company, Inc., vol. I, 1963; vol. II, 1964.

are missing. As she ponders this problem, she notices that window W is open. She looks out and realizes that the missing sugar cubes could be dissolved in the pond. This taxes her ingenuity, but she was once a nurse and knows how to test the pond for sugar. So she adds a new term to her formula, obtaining

$$\text{No. on floor} + \frac{\text{wt of box} - 4.3 \text{ oz}}{0.12 \text{ oz}} + k \text{ (sucrosity of pond)} = 37$$

and determines the proportionality constant k by tossing a cube into the pond herself.

This fixes up her formula, and again it works perfectly, accounting always for 37 sugar cubes. As she uses the formula, she begins to realize she could make her work easier if she dealt with *changes* in the various terms from one checking of the formula to the next. From this point of view the formula can be written as

$$\Delta(\text{No. on floor}) + \frac{\Delta(\text{wt of box})}{0.12 \text{ oz}} + k\,\Delta(\text{sucrosity of pond}) = 0$$

where the symbol "Δ" means *change of*. This equation simply says that if sugar cubes are conserved, the sum of all changes in the number of sugar cubes in various places must be zero. This equation too works perfectly for a long period, but one day it fails. The sum comes out not zero, but −4. Four sugar cubes are missing! This time it doesn't take mother long to notice that *both* windows are open and that she has no term in her equation to account for sugar cubes thrown out through window Q. She does not see any sugar cubes on the ground outside, but she does see several squirrels running about. How can she possibly keep track of all that goes on outdoors? The pond was bad enough, but what about squirrels and who knows what else? Her

husband, an electrical engineer, solves her problem by building a detection system at each window that counts the sugar cubes as they fly past, so it is no longer necessary to keep track of what happens outdoors. It is only necessary to record what passes through the walls of the room. The mother revises her formula again to reflect the new accounting procedure:

$$\Delta(\text{No. on floor}) + \frac{\Delta(\text{wt of box})}{0.12 \text{ oz}} + \text{No. passing } W + \text{No. passing } Q = 0$$

Note that we did not put Δ's with the two new terms. They need not be thought of as a *change* in anything. They just represent a number of objects passing a boundary during the interval between checks. In fact, we may as well simplify these terms to read W and Q. We can also transpose them to the other side of the equation; the result is

$$\Delta(\text{No. on floor}) + \frac{\Delta(\text{wt of box})}{0.12 \text{ oz}} = -Q - W$$

You see that we are getting more and more technical, and when this happens, technical terms also begin to appear. We may as well introduce several such terms here. Notice that we have narrowed our attention down to the room and to its walls, i.e., to a small region of space. In technical language, we call the room our *system*, and the walls become its *boundary*. Everything outside the boundary is called the *surroundings*. We would very much like to get rid of the surroundings because of their infinite complexity, but we can't really ignore them. On the other hand, we can make our formula *look* like it deals only with the system. The last form in which we wrote our formula puts the terms that have to do with changes in the system on the left. On the right we have terms to show what passes out of the system, but they are really there to account for changes in the surroundings. By associating them with the boundary of the system we make the appearance of dealing solely with the system. We treat Q and W as quantities, not as changes in anything, but in fact they are there to account for changes in the surroundings. Any conservation law must somehow include both the system and its surroundings. By insisting that we can account for the surroundings by counting at the system boundary, we are in fact adding something new to the content of a conservation law. It is a bit subtle but becomes obvious once pointed out. We do not expect one of Dennis' sugar cubes suddenly to disappear from his room on one side of the world and simultaneously to reappear someplace on the other side of the world, even though the other side is part of the surroundings. Why not? No simple statement of a conservation law excludes this. But it just isn't reasonable; it doesn't make sense. We'll leave it at that. The point is that the system-and-its-boundary formula excludes this possibility. We could also exclude it by insisting that conservation exists between a system and its local surroundings, but then we would have to define "local" as any part of the universe with which the system interacts. Then we would find it necessary to define "interacts," and so on. The beauty of the mathematical system-and-its-boundary formula is that it avoids this chain of verbiage, and this is one of the major advantages of the use of mathematics in the formulation of the laws of science, not that conservation of sugar cubes is a law of science—not yet, at any rate. So let's return to Dennis, his mother, and the 37 sugar cubes.

All is going well, except that Dennis' final sugar cube just entered the surroundings. It's time for a new game, and Dennis' mother dumps a handful of sugar cubes in his cigar box. This time she doesn't even count them. Can she still play the game? She certainly can, and she can even delay the start. All it takes is an initial observation and the setting of the window counters to zero. The formula always works, and when the counter on window Q breaks down, the mother realizes she can use her formula to find out how many sugar cubes are being fed to the squirrels.

Now consider another situation. A friend comes to visit and hands Dennis a bag of jelly beans. The mother doesn't happen to see this, and the friend says nothing about it. Furthermore, Dennis treats the jelly beans as if they were illegal; he never leaves any on the floor, and he won't say what he has. His mother is very curious, but all she knows is that Dennis has *something* in his cigar box. Nevertheless, she decides to try her formula; and it's going to work, because jelly beans come in lumps, and that's essential to her accounting scheme. Remember, she does not know what Dennis has. It is only necessary that she believe in lumps; she doesn't have to *see* them. She *does* have one problem; she does not know the weight of a lump. So her formula must be written

$$\frac{\Delta(\text{wt of box})}{a} = -Q - W$$

How does she get a, the weight of a lump? There's only one way; she must use her formula. So she weighs the box and sets the counters. Then after an interval she reweighs the box, records Q and W; now a is the only unknown in her formula, and she determines its value. After that she can use the formula to check her "law of conservation of lumps." Alternatively, she can use it to calculate any one of the three factors in it from the other two, provided only that she accepts the law of conservation of lumps to be valid.

Perhaps this is all absurdly obvious. If so, we can make it more cryptic by noting that the left-hand member of the mother's formula can be viewed a bit differently. This formula represents no more than a counting scheme, and Q and W represent counts directly. But the left-hand member is a count only indirectly. Clearly, the number of counts that it represents is given by the change in some *function of* the weight of the box. Thus the equation may equally well be written

$$\Delta[f(\text{wt of box})] = -Q - W$$

where $f(\text{wt of box}) = \dfrac{\text{wt of box}}{a}$

Here we know precisely the nature of the function f(wt of box), and by experiment we have established the value of a, the only adjustable parameter in it. However, we can imagine more complex situations where the function depends on properties of the box other than weight (perhaps on its electric charge or its permeability to x-rays). Moreover, the nature of the function may be far from simple. Thus we begin to see how a conservation law can become both difficult and abstract.

The law of conservation of energy is inherently more difficult and abstract because it does not deal with the conservation of lumps. Energy does not come in uniform lumps. This law proclaims the conservation of a number which does not represent any particular *thing*. Let's examine this in detail. How is energy conservation similar to and different from conservation of sugar cubes and jelly beans? They are alike in that the formulas which describe their conservation are mathematically similar; that is, the formulas include terms that account for changes in both the system and its surroundings. Moreover, their simplest and most convenient expression is given in terms of changes which occur within the system and in terms of quantities which pass the boundary of the system. This also requires that conservation be *local*. Thus we can write the same equation for energy conservation as we did for the conservation of lumps. It is analogous to the case in which we never saw the lumps, for nobody has ever claimed to *see* energy. The energy of a system is no more evident than jelly beans enclosed in a cigar box. So our conservation

formula has the form

$$\Delta(\text{energy of system}) = -\text{energy out by } Q - \text{energy out by } W$$

The energy of the system is presumed to be some function of the measurable properties of the system, just as the number of jelly beans was a function of the weight of the box. But we can't weigh energy, and the functional relationship is not known ahead of time. We can only *guess* of what property the energy of the system is a function. So we guess that it may be a function of temperature, pressure, composition, magnetization, etc. We really don't know so we'll leave it indefinite by writing

$$\text{Energy of system} = U(T,P,\text{etc.})$$

where we call U the *internal energy function*, and the parentheses show of what property it is a function. Our conservation formula is now written

$$\Delta[U(T,P,\text{etc.})] = -Q - W$$

The notation is often simplified still further so that we usually have

$$\Delta U = -Q - W$$

and we get careless with our terminology and call U simply the *internal energy*, as though we know exactly what we're talking about. But in fact we don't, and U is known only as a function of other things.

Q and W are terms representing energy passing the system boundary, not just by different windows, but by different modes. They are called *heat* and *work*, respectively, and both words have a special technical meaning. Both can give us all sorts of trouble, but for the moment let's assume we know all about them and can measure them.

You may be thinking that I have somehow *derived* the equation of energy conservation. Nothing could be further from the truth. I have just written it down. That's all anybody can do. No matter how much is written about this equation in thermodynamics texts, no matter how many fancy diagrams are drawn, no matter how confused the issue is made by mathematical manipulations, if you look carefully, you will find in the end that the author has merely written it down. No fundamental law of science is derivable by any means that we know today. If we could derive such laws, they would not be called fundamental. Then have I *explained* the law of conservation of energy? Again, I have not. I have tried to make the fact that it works seem plausible, but primarily I am trying to show you *how* it works, and there is a little way to go yet.

One thing about my equation may be bothering you. It is written with minus signs on both Q and W. The origin of these minus signs lies in the fact that Dennis could throw sugar cubes only *out of* the system. Had sugar cubes somehow come only *into* the system, both signs would be plus. However, the equation is usually written

$$\Delta U = +Q - W$$

This is just an accident of history. The first applications of thermodynamics were made to heat engines, devices which take *in* heat and put *out* work. The signs merely reflect a decision on the part of the founding fathers to make heat *in* and work *out* positive quantities for their favorite device. You can write it any way you want, that is, $+Q + W$, $-Q - W$, $-Q + W$, or $+Q - W$. All that is required is consistency in ascribing signs to your *numerical* values of Q and W. We will henceforth follow the crowd and write

$$\Delta[U(T,P,\text{etc.})] = Q - W$$

How is this equation to be used? For engineering purposes we want to use it to calculate either Q or W, or even both Q and W if we can find a second equation connecting Q and W. But how can we use it without knowing the functional relation $U(T,P,\text{etc.})$? How are we to get numbers for this function? How are we even going to find out what U is a function of?

The answer to the last question is easiest. It involves the notion of *state*. We say that the internal state of a system is fixed when none of its measurable properties changes any more. Then the problem is to find what measurable properties we need to establish at arbitrary values in order to fix the state of a system. This is one of the major complications of thermodynamics—to know what the variables are. The only way to find out is by experiment. The internal energy is presumed to be a function of the same variables as is the volume.

Having established the variables, say temperature T and pressure P, how do we get the relationship between U and these variables? This is the second major complication of thermodynamics. We find in any ultimate analysis that we must use our equation of energy conservation. This may seem incredible; after all, the use of the equation

$$\Delta[U(T,P)] = Q - W$$

is to find Q or W. How can we use it to calculate values for $U(T,P)$ and Q or W at the same time? The secret is that we don't do both *at the same time*. We play the game forward and backward, but at different times, just as Dennis' mother did when she used her equation backward to determine the weight of a jelly bean or lump that she never saw. Having done that, she could subsequently use her equation forward to check on the conservation of lumps or to find the number of lumps in the pond or the number fed to the squirrels. The same thing holds true for the energy equation, except that the process is more complicated because not only do we never see the energy, it does not come in lumps.

In the laboratory we set up a small system and make changes in it, measuring T and P and Q and W. From these it is possible to deduce $U(T,P)$ for various values of T and P within an additive constant. In use we always have $\Delta[U(T,P)]$ so that the constant drops out. We can put down $U(T,P)$ in the form of a graph, a table, or an equation. But we must *have* such information, and it must ultimately come from experiment. Moreover, we must have $U(T,P)$ or $U(T,P,\text{etc.})$ for the particular kind of system we wish to deal with. Given this information, we may apply the energy formula

$$\Delta[U(T,P,\text{etc.})] = Q - W$$

to any process involving the same kind of system, and it is in no way limited to just those processes used to determine $U(T,P,\text{etc.})$. Any such limitation would make it of no use at all.

Let us say that we know $U(T,P,\text{etc.})$ and now apply our conservation formula to many different processes. We find time after time that it checks out, that it works. Then one day it doesn't. What to do? We do just what Dennis' mother did. We look for sugar cubes under the rug, in the pond, or in any place we had not considered before. We notice that our system changed its elevation. Maybe that changes its energy. Sure enough, a bit of experimentation shows that we can devise a potential energy function which fixes our formula—for a time. We go through the whole business again and find we need a kinetic energy function when the system has velocity. So we add terms to our formula as follows:

$$\Delta[U(T,P,\text{etc.})] + \Delta[\text{PE}(z)] + \Delta[\text{KE}(u)] = Q - W$$

Fortunately, the two new functions are known explicitly in terms of measurable properties; thus

$$\text{Potential energy function} = \text{PE}(z) = mgz$$

$$\text{Kinetic energy function} = \text{KE}(u) = \tfrac{1}{2}mu^2$$

where z = elevation
m = mass
g = acceleration of gravity
u = velocity

Thus

$$\Delta[U(T,P,\text{etc.})] + mg\,\Delta z + \tfrac{1}{2}m\,\Delta u^2 = Q - W$$

And so it goes. Whenever our equation does not work, we can fix it up with a new term. Others may object that this isn't fair and accuse us of deciding arbitrarily that the law of conservation of energy *is* valid and of being *determined* to make it work. They claim that we doctor it up so that everything comes out all right. They would, of course, be correct if we ever added a term called "unaccounted for" or "lost." That would spoil it all. But it turns out that every time we add a new term to our equation, we're also able to say how to evaluate it from measurable parameters. This sort of doctoring is completely justified. Can we do the same thing with a law of conservation of sugar cubes? The answer is no. What if Dennis stomps on a sugar cube? We still have sugar but no cube. Or he may eat one, and then we don't even have sugar.

Perhaps the ultimate test of our accounting scheme came with the advent of nuclear fission. Energy appears in this case to come from nowhere, but in fact a term provided by Einstein readily maintains the validity of the conservation equation. The new term is a nuclear energy function, and its change is $-c^2\,\Delta m$, where c is the velocity of light and Δm is the change in mass of the system. The minus sign is necessary because Δm is negative; the mass of the system decreases. Our equation then becomes

$$\Delta[U(T,P,\text{etc.})] + mg\,\Delta z + \tfrac{1}{2}m\,\Delta u^2 - c^2\,\Delta m = Q - W$$

When we're all done, what do we have? We have an equation which is said to give *mathematical* expression to the law of conservation of energy. But how else could this law be expressed except mathematically? Every form of energy we have discussed is known *only* as a function of other variables, and I have been careful to say internal energy *function*, potential energy *function*, etc. Functions are *pencil-and-paper* constructs. I can't show you a function that has any other substance, and that is why I can't show you a chunk of energy or why I can't define it or tell you what it is. It is just mathematical or abstract or just a group of numbers. Thus we have no energy meters, no device we can stick into a system which will record its energy. The whole thing is man-made.

What we have is a scheme with a set of rules. The scheme involves only changes in the energy functions. It is set up this way because we have no way to calculate absolute values of our energy functions. The remarkable thing about this scheme is its enormous generality. It applies equally to the very small and to the very large; it applies over any time interval, short or long; it applies to living matter as well as to dead. It applies in the quantum-mechanical and relativistic realm as well as in the classical. It just plain works. We can never be absolutely sure that it will always work, but we are sufficiently confident so that with it we make all sorts of predictions, and that is its use.